In situ efficient growth of Rubik nanocube WO$_3$·0.33H$_2$O array films for high-performance electrochromic energy storage devices

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Tungsten trioxide (WO$_3$)-based electrochromic devices have attracted considerable attention due to their promising applications in smart windows, energy-efficient displays, and sunglasses. However, it is still challenging to fabricate high-performance WO$_3$ electrochromic films using an efficient and facile wet method. Here, we report a one-step strategy for the in situ growth of WO$_3$·0.33H$_2$O Rubik nanocube films on fluorine-doped tin oxide (FTO) conducting substrates in hydrogen peroxide (H$_2$O$_2$) and an ethylene glycol (EG)-containing hydrothermal system that is seed layer-free. The complexing effect of H$_2$O$_2$ results in the highly efficient formation of WO$_3$·0.33H$_2$O films with good interface stability and a porous structure formed by the stacked Rubik nanocubes. Benefiting from the porous structure, the obtained WO$_3$·0.33H$_2$O film delivers outstanding electrochromic and electrochemical energy storage performance, such as large optical modulation over the wide-band visible-near-infrared (Vis-NIR) range (up to 80% at 633 nm and 90% at 1000 nm), high coloration efficiency (65.6 cm$^2$ C$^{-1}$), high rate capability as well as good cycling stability (with 80% transmittance retention over 1000 cycles). Furthermore, as a demonstration, a complementary electrochromic device was assembled based on the WO$_3$·0.33H$_2$O film, which offers a high coloration efficiency (92.6 cm$^2$ C$^{-1}$), optical modulation in the visible range (up to 70% at 633 nm), and large energy storage of 27.4 mA h m$^{-2}$ at 0.07 mA cm$^{-2}$. We believe that this efficient and facile wet method for preparing electrochromic films will provide a fresh approach to investigating high-performance electrochromic systems.

**Introduction**

Electrochromic devices can reversibly change their optical properties (e.g. transmittance, absorptivity, and reflectivity) under small voltages, which has sparked considerable interest in the fields of smart windows, anti-glare mirrors, and smart displays. For instance, electrochromic smart windows dynamically control the visible-near-infrared (Vis-NIR) light by switching between their transparent and opaque states, efficiently regulating indoor comfort in buildings and vehicles. The electrochromic film generally dominates the performance of the device, which is recognized as an indispensable component of the device. In this case, various electrochromic materials have been widely studied, including transition metal oxides (TMO), conducting polymers and viologen. In particular, tungsten oxide (WO$_3$), as one of the representative TMO materials, offers many advantages, such as large optical modulation and good environmental stability against high temperatures and solar radiation. Nevertheless, it is still challenging to develop efficient and facile wet methods that enable the fabrication of WO$_3$ materials with both high optical modulation and long cycling stability.

To date, a range of wet methods has been used for the attempted fabrication of WO$_3$ films, including chemical bath deposition, electrodeposition, hydrothermal, solvothermal and sol–gel methods. Among them, the hydrothermal technique offers attractive opportunities for fabricating WO$_3$ films with various crystal structures and morphologies. It is worth noting that the lattice mismatch between WO$_3$ and substrates generally causes film fabrication to fail. To solve this problem, the seed layer (e.g. WO$_3$ and titanium dioxide (TiO$_2$)) was generally pre-prepared on the substrate to trigger the growth of WO$_3$ films in the hydrothermal method. For instance, Guo et al. described the growth of WO$_3$ films induced by the TiO$_2$ seed layer in a hydrothermal environment, resulting in...
in large optical modulation of 73.45% and high cyclic stability of the film. Another solution is the direct growth of WO₃ films on the substrate using organic molecules (e.g. citric acid, ethylene glycol, glycerol). The hydroxyl group in molecules was employed to promote the bridge between WO₃ nuclei and substrates. For instance, Jia et al. described the unique glycerol-assisted growth of WO₃ films with coral-like nanostructures in a hydrothermal system. This nanostructure significantly improved the electron/ion transport rate and cycling stability of the film. Nevertheless, there are still some limitations that hinder the commercial applications of WO₃-based electrochromic films, such as high hydrothermal temperatures approaching 200 °C, long reaction times (several hours), and even complex fabrication procedures. Therefore, it is necessary to explore a novel hydrothermal system that can easily and efficiently promote the fabrication of high-performance WO₃ electrochromic films.

In this work, we developed a one-step fabrication strategy for the in situ growth of WO₃·0.33H₂O films on fluorine-doped tin oxide (FTO) conducting substrates using hydrogen peroxide (H₂O₂) as the green complexing agent and ethylene glycol (EG) as a bridging agent. Benefiting from the efficient modulation of the film growth by the synergistic effect of H₂O₂ and EG, the obtained WO₃·0.33H₂O films only undergo a short-term and low-temperature fabrication process and display a uniform Rubik nanocube structure with excellent electrochromic and electrochemical energy storage performance, including large optical modulation over the wide-band Vis-NIR range, high coloration efficiency, high areal capacity, and good cycle stability. Furthermore, a prototype of the complementary electrochromic device was assembled using WO₃·0.33H₂O and Prussian white (PW) films, demonstrating its powerful electrochromism and energy storage functions. This work provides a facile and highly efficient strategy for the one-step growth of WO₃·0.33H₂O Rubik nanocube films with strong substrate adhesion, which provides a distinctive pathway for the preparation of other electrochromic optoelectronic films.

Results and discussion

Here, a WO₃·0.33H₂O Rubik nanocube film was prepared in the short-term (45 min) by the hydrothermal method at a low temperature (120 °C), and the new role of H₂O₂ and EG in efficiently modulating the WO₃ film growth on FTO substrates was explored (the detailed process is given in the Experimental section). X-ray diffraction (XRD) patterns were first collected to determine the crystal structures and phases of the WO₃ films. With the assistance of H₂O₂ and EG, the obtained film exhibits the diffraction peaks at 14.11, 18.1, 23.1, 24.18, 27.16, 28.30, and 36.80°, in consonance with the (020), (111), (002), (200), (131), (220) and (222) planes of orthorhombic WO₃·0.33H₂O (JCPDS no. 35-270), respectively (Fig. 1(a)). The other diffraction peaks correspond to SnO₂ (JCPDS no. 46-1088). In contrast, it is difficult to trigger the growth of WO₃·0.33H₂O films in the absence of H₂O₂ or EG with a growth time of even up to 30 h (Fig. S1, ESI†). X-ray photoelectron spectroscopy (XPS) was further performed to evaluate the surface chemical composition and oxidation state of the as-prepared WO₃·0.33H₂O. The total survey spectrum of the WO₃·0.33H₂O film confirms the existence of W, O and C (Fig. 1(b)), revealing the purity of the obtained films. The XPS spectrum of W 4f contains three characteristic peaks at 35.9 eV for W 4f₇/₂, 38.1 eV for W 4f₅/₂ and 41.5 eV for W 5p₃/₂ (Fig. 1(c)), which are ascribed to the binding energy of W⁶⁺. The high-resolution spectrum of O 1s in Fig. 1(d) reveals that the two peaks at 530.5 and 532.5 eV are related to the oxygen lattice (W=O and W−O−W bonds) and the hydroxylation of crystalline hydrate in the WO₃ film, respectively. These results further confirm the successful preparation of WO₃·0.33H₂O films in H₂O₂ and the EG-contained hydrothermal system.

Scanning electron microscopy (SEM) images show that a large number of stacked Rubik nanocubes (<100 nm) and irregular nanoscale pores were uniformly formed in situ on the FTO substrate, and a WO₃·0.33H₂O film with a thickness of about 630 nm firmly adhered to the surface of the substrate (Fig. 2(a) and (b)). In addition, energy dispersive spectroscopy (EDS) analysis demonstrated a homogeneous elemental distribution of W and O atoms throughout the tested areas of the WO₃·0.33H₂O film (Fig. S2, ESI†). Note that the obtained WO₃·0.33H₂O film exhibits strong adhesion with the FTO substrate, as the edges of the scratch remained almost unchanged during the tape adhesion/peeling test on the film (Fig. S3, ESI†). The introduction of H₂O₂ and EG molecules is conducive to the formation of WO₃·0.33H₂O Rubik nanocube films with a large specific surface area, porous structure, and tight binding of the FTO substrate, facilitating ion and electron transport in the electrochromic process. High-resolution transmission electron
microscopy (HR-TEM) further confirms that the spacing of the lattice fringes of WO$_3$·0.33H$_2$O Rubik nanocube films is ~0.63 nm (Fig. 2(c)), corresponding to the (020) crystallographic planes of WO$_3$·0.33H$_2$O with the orthorhombic phase. The interplanar spacing is larger than the lithium-ion radius. A larger lattice spacing promotes the insertion and extraction of ions to optimize the response time of the film.

The formation process of the orthorhombic WO$_3$·0.33H$_2$O film is schematically illustrated in Fig. 2(d), in which the growth principle of the WO$_3$·0.33H$_2$O film can be explained according to the following reactions:

1. \[ H_2WO_4 + 2H_2O_2 \rightarrow H_2[WO(O_2)_{2}(OH_2)](PTA) + H_2O \]  
2. \[ H_2[WO(O_2)_{2}(OH_2)] \rightarrow [WO(O_2)_{2}(OH_2)]^{2-} + 2H^+ \]  
3. \[ [WO(O_2)_{2}(OH_2)]^{2-} + 2H^+ \rightarrow WO_3 \cdot 0.33H_2O(nucleus) + O_2 + 1.67H_2O \]  
4. WO$_3$·0.33H$_2$O (nucleus) \( \rightarrow \) WO$_3$·0.33H$_2$O (nanocubes)  

In the initial state of film formation, the precursor tungstic acid is complexed with peroxo-ligands [O$_2$]$^{2-}$ in H$_2$O$_2$ to form strongly acidic peroxytungstic acid (PTA). WO$_3$·0.33H$_2$O crystal nuclei can be obtained when PTA is decomposed (formula (3)). In this process, WO$_2$(OH)$_2$ is first precipitated from PTA and subsequently hydrated into two types of supersaturated WO(OH)$_4$(OH$_2$) and W(OH)$_6$ under acidic conditions. The nucleation and growth of WO$_3$·0.33H$_2$O is then triggered by the formed six-membered ring structure that consists of WO(OH)$_4$(OH$_2$) and W(OH)$_6$.[36,45] The hydroxyl groups of the EG molecule can bridge the WO$_3$·0.33H$_2$O nuclei with the FTO surface, causing an even distribution of WO$_3$·0.33H$_2$O on the FTO substrate. To verify the effect of H$_2$O$_2$ in the WO$_3$·0.33H$_2$O film formation process, we compared the acidic conditions of various precursor solutions, showing that the solution with H$_2$O$_2$ exhibits a lower pH value of 1.25 than that of the sample without H$_2$O$_2$ (1.72). Similarly, a thin film was also obtained on the FTO substrate after adjusting the pH of the PTA precursor solution to 1.25 using hydrochloric acid (Fig. S4, ESI†). This reveals that the H$_2$O$_2$ in this reaction system not only supports the formation of PTA precursor via the complexation of tungstic acid and peroxo-ligands, but also stabilizes PTA at certain concentrations from condensing into by-product “polytungstic species” and contributes to the production of adequate H$^+$ protons to supersaturate the monomers of WO(OH)$_4$(OH$_2$) and W(OH)$_6$ for the nucleation of WO$_3$·0.33H$_2$O.

In order to evaluate the electrochemical and electrochromic performance of the WO$_3$·0.33H$_2$O Rubik nanocube films, cyclic voltammetry (CV) measurements were carried out at a scan rate of 20 mV s$^{-1}$ within the potential window of −1 to 1 V (vs. Ag$^+$/Ag) using a three-electrode system in 1 M LiClO$_4$/PC electrolyte; Meanwhile, the transmittance change during the electrochromic process at a wavelength of 633 nm was real-time recorded.
by in situ dynamic spectroscopy (Fig. 3(a)). The electrochromic process of WO$_3$·0.33H$_2$O is accompanied by intercalation and deintercalation of Li$^+$ ions as follows:

$$\text{WO}_3 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{WO}_3$$  \hspace{1cm} (5)

During the cathodic polarization process, the WO$_3$·0.33H$_2$O film undergoes a typical reduction process and its transmittance decreases simultaneously from a transparent state to a navy blue colored state. The transmittance change can be attributed to the efficient Li$^+$ ion intercalation of WO$_3$·0.33H$_2$O, leading to the valence transformation of W elements from W$^{6+}$ to W$^{5+}$. Inversely, the effective deintercalation of lithium ions in the anodic polarization process leads to the valence transformation of W$^{5+}$ to W$^{6+}$ and the bleaching process from the colored state to the initial transparent state. The closed coloration and bleaching curves demonstrate that the WO$_3$·0.33H$_2$O film exhibits excellent electrochromic reversibility.

As a crucial parameter of light regulation capability, the optical modulation ($D_T = T_b/T_c$, where $T_b$ and $T_c$ are the transmittances in the bleached and colored states) of the WO$_3$·0.33H$_2$O film was further examined over the wavelength range of 300–1300 nm under different potentials (Fig. 3(b)). By applying increased reduction potentials from −0.2 to −1 V (vs. Ag$^+/Ag$), the spectra show a decreasing transmittance in both Vis-NIR bands, corresponding to the color change from transparent to opaque (Fig. S5, ESI†). When a reduction potential of −1 V (vs. Ag$^+/Ag$) was applied to the film, a very low transmittance of 11.6% at a wavelength of 633 nm and an impressive transmittance of ~1% close to the limit in the NIR range from 900 to 1300 nm was achieved by the WO$_3$·0.33H$_2$O film. At an oxidation potential of 1 V (vs. Ag$^+/Ag$), the WO$_3$·0.33H$_2$O film is transparent in the Vis-NIR range. The WO$_3$·0.33H$_2$O film delivers large optical modulation of 80% at 633 nm and 90% at 1000 nm, with the values being much higher than those reported in most previous works.$^{36,41,51}$

The in situ dynamic transmittance of the WO$_3$·0.33H$_2$O film was measured by applying potentials of −1 to 1 V (vs. Ag$^+/Ag$) at a wavelength of 633 nm (Fig. 3(c)). The response time refers to the time required for a 90% transmittance change between the switching of coloration and bleaching states, which is an important parameter for evaluating the reaction kinetics of electrochromic films. The coloration ($t_c$) and bleaching ($t_b$) times were calculated to be 15 and 14 s, respectively. In addition, coloration efficiency (CE) generally reflects the energy-saving condition of the electrochromic film, which is defined as the optical density change ($\Delta\text{OD}$) in response to the per unit charge ($\DeltaQ$) inserted into the electrochromic film.$^{52}$ It can be expressed by the following equation:

$$\text{CE} = \frac{\Delta\text{OD}}{\DeltaQ} = \frac{\log(t_b/t_c)}{\DeltaQ/A}$$  \hspace{1cm} (6)

where $A$ is the active area of the film. According to the slope of the linear region of the $\Delta\text{OD}$ variation at different current densities (Fig. 3(d)), the CE of the WO$_3$·0.33H$_2$O film was calculated to be approximately 65.6 cm$^2$ C$^{-1}$ at 633 nm, which...
is higher than that of porous WO₃ films fabricated using a similar hydrothermal method with the assistance of a structure-directing agent. This high CE value suggests that our fabricated WO₃-0.33H₂O film can achieve large optical modulation by consuming a small amount of charge. In addition, the electrochemical cycling stability of electrochromic films is a critical parameter, which determines their practical application. In order to test the durability of the film, the cycling performance of the WO₃-0.33H₂O film was further investigated by alternately applying coloration and bleaching potentials of −1 and 1 V (vs. Ag⁺/Ag), respectively (Fig. 3(e)). It was found that the film maintained ~80% of its primary optical modulation even after 1000 cycles. The good cycling stability was attributed to the strong interface compatibility between the film and substrate. In order to better understand the charge storage kinetics of the Rubik nanocube film, the Li⁺ ion storage mechanism was analyzed by employing a series of redox peaks in the CV curves at different scan rates from 5 to 60 mV s⁻¹ (Fig. S6, ESI†). The b-value obtained from the log(𝑖) against log(𝑣) plots is 0.67 (eqn (S1), ESI†), verifying that the electrochemical process was mainly dominated by the diffusion behavior with the intercalation-deintercalation of ions in the WO₃ lattice. We also compared the electrochromic properties of our WO₃-0.33H₂O film with other films prepared by hydrothermal methods, and found that our film displayed superior efficiency in film formation at only 120 °C for 45 min, large optical modulation as well as outstanding cycling stability (Table S1, ESI†).

The electrochromic process of the WO₃-0.33H₂O film is generally synchronous with energy storage due to the same redox reaction they followed. Therefore, it is expected that the film not only exhibits potential electrochromic functions but also delivers an electrochemical energy storage function. To characterize the performance of energy storage capability, galvanostatic charge–discharge (GCD) measurements were carried out at different current densities in a potential window of −1 to 0 V (vs. Ag⁺/Ag) (Fig. 4(a)). The symmetric shapes of the GCD curves with a negligible IR drop indicate the high Coulombic efficiency and electrochemical reversibility of the WO₃-0.33H₂O film. The increased current density leads to a shortening of the GCD time, which is caused by the relatively insufficient participation in the redox reaction of the electrode with Li⁺ ions. Accordingly, the specific areal capacities of the film are calculated to be 17.9, 15.6, 15.1, 14.3 and 13.7 mAh cm⁻² at the current densities of 0.07, 0.1, 0.14, 0.17 and 0.24 mA cm⁻², respectively (eqn (S2), ESI†). Besides, in situ transmittance spectra with the GCD process were further detected at a single wavelength of 633 nm to verify the visualization of energy storage (Fig. 4(b) and (c)). At a high galvanostatic current density of 0.24 mA cm⁻² in the charging process, the WO₃-0.33H₂O film can achieve almost the same optical modulation as the constant voltage charging potential of −1 V (vs. Ag⁺/Ag). In the discharging process, this film can completely return to the transparent bleached state. The IR drop existing in the discharging curve is ascribed to the internal resistance of the film when a high current passes through it, causing the actual discharge voltage of the film to be lower than the charge voltage. The WO₃-0.33H₂O film demonstrates a superior real-time electrochromic display for energy storage. Such an attractive visualization capability of the film would promote the potential application of an energy storage indicator based on electrochromism. Furthermore, the areal capacity and optical modulation of the WO₃-0.33H₂O film at different current densities are summarized in Fig. 4(d). The optical modulation of the WO₃-0.33H₂O film remains almost unchanged as the variation trend of current density from 0.07 to 0.24 mA cm⁻², demonstrating its excellent rate performance.

Considering the excellent electrochromic and energy storage properties of the WO₃-0.33H₂O film, a complementary type of electrochromic energy storage device (EESD) was designed and assembled by integrating a PW electrode with the functions of electrochromism and ion storage (Fig. 5(a)). During the coloration of the WO₃-0.33H₂O film, the transparent PW film can be transformed into a blue Prussian blue (PB) film. The PW films deliver optical modulation (77%) at 633 nm over a potential window of −0.5 to 0.5 V (vs. Ag⁺/Ag) and a fast response time (1.9 s for coloring and 8.6 s for bleaching) (Fig. S7, ESI†). The in situ transmittance spectrum of the assembled EESD was obtained during CV scanning at 20 mV s⁻¹ in a potential window of −3.5 to 2 V. The transmittance of the WO₃-0.33H₂O film dynamically reduces with increasing voltage from −3.5 to 2 V, and then returns to its initial state when the voltage returns to −3.5 V, reflecting good electrochemical reversibility of this assembled EESD (Fig. S8, ESI†). Moreover, the EESD displays large optical modulation in a broad optical spectrum range such as 71% and 58% at 633 nm and 1000 nm, respectively (air as the transmittance baseline, Fig. 5(b)). Optical modulation in the visible region is realized by the synergistic contribution of the WO₃-0.33H₂O electrode and PW counter electrode, whereas optical modulation in the NIR region mainly...
originates from the contribution of the WO$_3$·0.33H$_2$O electrode. Furthermore, we converted the optical transmittance spectra to solar irradiance spectra in the 300–1300 nm region based on the actual solar transmittance (Fig. S9, ESI†). The integral area of the transmittance curve of the device in the bleached and colored states accounts for 72% and 8% of the total solar radiation curve (AM 1.5G) respectively, demonstrating a large solar radiation modulation of 64% in practical applications. By alternately applying voltages of 2 and −3.5 V, the EESD can achieve a fast coloration response of 8 s due to the synergistic electrochromism of WO$_3$·0.33H$_2$O and PW electrodes (Fig. 5(c)). Benefiting from the complementary design of the devices and the synergistic effect of the film, the EESD possesses an impressive CE of 96.7 cm$^2$C$^{-1}$, which is desirable for electrochromic applications (Fig. 5(d)). Notably, along with the GCD processes at 0.07 mA cm$^{-2}$ (Fig. 5(e)), the EESD shows reversible color variation with optical modulation of 64% at 633 nm. Furthermore, two colored EESDs connected in series supply power to the digital timer over 42 minutes, illustrating the superior energy storage performance of the EESD (Fig. 5(f)). Therefore, such assembled EESD has excellent bifunctional properties of energy storage and electrochromism, which is extremely important for energy-saving applications such as energy-saving buildings and smart energy-efficient devices.

**Conclusions**

We proposed a novel strategy for the *in situ* fabrication of WO$_3$·0.33H$_2$O films on the FTO substrates by employing H$_2$O$_2$ as a hydrothermal method. The synergistic effect of H$_2$O$_2$ and EG can efficiently facilitate the fast growth of WO$_3$·0.33H$_2$O Rubik nanocube films with strong substrate adhesion in a short green complexing agent and EG as a bridging agent in the reaction time (45 min). Such WO$_3$·0.33H$_2$O Rubik nanocube films exhibit excellent electrochromic performances, including high optical modulation over the Vis-NIR range (up to 80% at 633 nm and 90% at 1000 nm), high coloration efficiency (65.6 cm$^2$C$^{-1}$), good rate capability as well as long-term electrochemical stability with 80% transmittance retention over 1000 cycles. In addition, a smart complementary EESD with functions of energy storage and electrochromism was assembled based on WO$_3$·0.33H$_2$O and PW electrodes, showing comparable bifunctional performance of electrochromic and energy storage.

We believe that the study of the green complexing agent of H$_2$O$_2$ will make a unique contribution to the development of high-performance multifunctional smart electrochromic devices.

**Experimental section**

**Materials**

Tungstic acid (H$_2$WO$_4$), ethylene glycol (EG, C$_2$H$_4$O$_2$, 99.8%), absolute ethyl alcohol (CH$_3$CH$_2$OH), lithium perchlorate (LiClO$_4$, ≥95.0%), propylene carbonate (CH$_3$CHCH$_2$CO$_3$, PC, ≥99.7%) and hydrogen peroxide (H$_2$O$_2$, 30%) were purchased from Sigma-Aldrich. All reagents were used as received without further purification, and deionized water (DI water) was prepared using a water purifier (Milli-Q 18 MΩ, Millipore Corp).
Fluorine-doped tin oxide (FTO)-coated transparent conductive glass (sheet resistance: ~14 Ω, thickness: ~2.2 mm) was purchased from Zhuhai Kaivo Electronic Components Co., Ltd.

Preparation of electrochromic WO₃·0.33H₂O films
The WO₃·0.33H₂O film was directly grown on FTO-coated glass substrates using a facile hydrothermal method. Briefly, 2.5 g H₂WO₄ was mixed with 10 mL H₂O₂ and 20 mL DI water under stirring at room temperature for 1 h, followed by transfer to an oil bath at 90 °C for 3 h until transparent light yellow peroxotungstic acid (PTA) was formed. To conveniently study the role of H₂O₂ in WO₃·0.33H₂O nuclei formation, we further removed excess hydrogen peroxide using a platinum sheet after synthesizing PTA, ensuring the quantitative analysis of H₂O₂. Afterward, the hydrothermal precursor of the WO₃·0.33H₂O films was obtained by diluting 6 mL PTA and 2.2 mL EG in 16.8 mL DI water, followed by adding 5 mL H₂O₂. FTO substrates with a sheet resistance of ~14 Ω sq⁻¹ were cleaned by ultrasonic treatment with acetone, deionized (DI) water, and ethanol in an ultrasonic bath for 15 min. The mixed solution was then transferred to a Teflon-lined stainless steel autoclave. The non-conductive surface of the FTO substrate (2 cm × 5 cm) was placed inside and inclined upward to support the growth of the film at 120 °C for 45 min. After the autoclave was cooled to room temperature, the substrate was rinsed several times with deionized water and dried in ambient air at 120 °C for 2 h.

Fabrication of PB films
PB films were electrodeposited onto FTO substrates according to a previously reported work. Briefly, the PB precursor for electrodeposition involved 0.66 g K₃[Fe(CN)₆], 0.32 g FeCl₃, 0.75 g KCl, and 100 mL DI water. The electrochemical deposition of the cathode was carried out using a three-electrode electrochemical system, in which FTO substrates served as the working electrode, a platinum sheet as the counter electrode, and Ag/AgCl as the reference electrode. A current density of 50 μA cm⁻² was applied to perform the electrodeposition of PB films for 400 s. Finally, the as-prepared PB films were flushed with water several times and dried at 60 °C for 1 h.

Assembly of the electrochromic energy storage device
The PW film was first obtained by electrochemical oxidation of the PB film under a potential of ~0.5 V. A complementary electrochromic energy storage device was then assembled using a WO₃·0.33H₂O Rubik nanocube film as the working electrode, a PW film as the counter electrode, and 1 M LiClO₄ in PC as the electrolyte. A clear double-sided adhesive tape (VHB4010, 3 M) with a thickness of 1 mm as the spacer was placed between the negative and positive electrodes. The device was sealed with an epoxy glue to prevent the leakage of electrolytes.

Characterization
The crystal structures and phase compositions of the films were determined by X-ray diffraction (XRD) using a Bruker AXS D8 Advance X-ray diffractometer. The morphology and elemental distribution of the films were characterized by field emission scanning electron microscopy (FESEM) associated with energy dispersive spectroscopy (EDS) mapping on a Navo NanoSEM 450. The lattice fringes of WO₃·0.33H₂O were confirmed by high-resolution transmission electron microscopy (TEM) on a JEM-2100. The element valences of the samples were determined using an AXIS ULTRA Imaging X-ray photoelectron spectroscope (XPS).

Electrochemical and electrochromic characterization
The electrochemical measurement of the WO₃·0.33H₂O film was carried out in a standard three-electrode system using an electrochemical workstation (PGSTAT 302N potentiostat, Autolab), in which the WO₃·0.33H₂O film, Pt wire, and Ag wire served as the working electrode, counter electrode, and reference electrode, respectively. The counter electrode was utilized to provide a platform for current transfer, while the reference electrode was used to measure the potential of the working electrode. In situ optical transmission spectra were collected using an ultraviolet-visible-near-infrared (UV-Vis-NIR) spectrophotometer (SHIMADZU UV-3600 plus). All samples were prepared in 1 M LiClO₄/PC electrolytes.

Notes and references
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